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Antisites in silicon carbide

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Ten years ago, deep-level-transient-spectroscopy (DLTS) signals, assigned to centers labeled as $H1$, $H2$, $H3$, and $E2$, have been detected in neutron-irradiated 3C SiC. The H centers were believed to be the primary point defects and the $E2$ center a secondary defect, which forms after the H centers start to migrate. A conclusive identification of these signals has not been presented so far. We present computational evidence that the H centers are due to silicon antisite defects (Si_C). In both cubic (3C) and hexagonal (2H) polytypes, the silicon antisite has several ionization levels in the band gap. The positions of these ionization levels in 3C SiC have been calculated accurately with the plane wave pseudopotential method using a large 128-atom site supercell, and compared with the DLTS spectrum. A very good agreement with experimental data indicates that H centers are due to the formation of Si_C during neutron irradiation. The formation energies and local geometries of the antisite defects in SiC are also reported. [S0163-1829(98)06708-3]

The development of silicon-carbide-based semiconductor devices has recently become a subject of intense research motivated by several superior characteristics of silicon carbide (SiC).[1,2] Yet, the applications of SiC have been hampered because of the difficulties confronted in the growth process of high-quality large-area crystals. For the characterization and identification of defects in SiC, several photoluminescence (PL),[3,4] electron spin resonance (ESR),[5,6] optically detected magnetic resonance (ODMR),[7,8] deep-level-transient-spectroscopy (DLTS), (Ref. 9) and positron annihilation spectroscopy (PAS) (Refs. 10,11) measurements have been performed. Native defects in SiC have been studied theoretically with both tight-binding[12,13] and *ab initio*[14,15] methods without, however, full three-dimensional (3D) relaxations. Recently, a pseudopotential study[16] has reported the formation energies and ionic relaxations for the neutral, singly positive, and negative vacancies in SiC. In the earlier theoretical studies, it was concluded that while antisites have low formation energies,[14] neither Si_C nor C_{Si} antisites have ionization levels in the band gap.[12–14] Since it is very difficult to detect electrically inactive defects experimentally, most of the observed spectra are explained in terms of vacancies, divacancies, di-interstitials, or other defect complexes. Only few native defects, namely, the carbon and silicon vacancy, are recognized from experiments.[5,6,17] So far, antisites have not been identified from the experimental data, whereas they are expected to be produced by irradiation or upon annealing after irradiation.[6] In this report, we present computational results for antisites in SiC, and argue that they indeed are responsible for several experimental observations.

The concentrations of defects in thermodynamical equilibrium are largely determined by their formation energies, with minor contributions from the phonon entropy. In order to gain information about the equilibrium concentrations and ionization levels of native defects, we have calculated the formation energies of and atomic relaxations around vacancies, antisites, and interstitials. The antisites C_{Si} and Si_C were studied in cubic and hexagonal SiC in all of their possible charge states. More complex polytypes (4H, 6H) can be considered as combinations of cubic and hexagonal lattices.

Our calculations are based on the density-functional theory (DFT) with the electron exchange correlation treated in the local density approximation (LDA).[18] We have used a Car-Parrinello–like pseudopotential approach.[19] For the C ion, the Vanderbilt-type ultrasoft pseudopotential[20] has been employed in order to reduce the number of plane waves needed to describe the electronic wave functions. Good convergence with respect to the basis set size was obtained already at a 20 Ry kinetic energy cutoff, which has been used in this work. A standard norm-conserving Bachelet-Hamann-Schlüter pseudopotential[21] has been used for the Si ion. The initial atomic configurations have been randomized slightly from the ideal structure to remove any spurious symmetries. All the ions in the supercell have been allowed to relax without any symmetry constraints. Most of the calculations are performed for a 128-atom-site supercell. In calculations for 2H SiC and interstitials a 32-atom supercell has been employed. Even the smaller supercell size has been shown[22] to give well-converged results provided that a proper **k**-point set[23,24] is used and that the average potential correction[25,26] is taken into account in the formation energy analysis. The average potential correction is also applied in the case of the 128-atom-site supercell. For the smaller supercell a 25 Ry kinetic energy cutoff is used. The formation energies have been calculated using the standard method.[25,26] Our values for the formation energies of neutral native defects are consistent with the recent *ab initio* calculations.[15,16] Further computational details can be found in Ref. 22.

Ten years ago, Nagesh *et al.*[27,28] reported DLTS measurements, where they observed defects in neutron-irradiated 3C-SiC. They found point-defect related centers labeled $H1$, $H2$, $H3$, and $E2$.[28] The electronic levels of the H centers are situated at 0.18 eV ($H1$), 0.24 eV ($H2$), and 0.514 eV ($H3$) above the valence band maximum, whereas the electron trap $E2$ is located 0.49 eV below the conduction band minimum. It was noticed that 90% of these defect centers produced by neutron irradiation were removed by annealing at 350 °C,[27] and a strong correlation between the progressive increase of the $E2$ defect concentration and the annealing of H centers was found.[27] Apparently the H centers are primary point

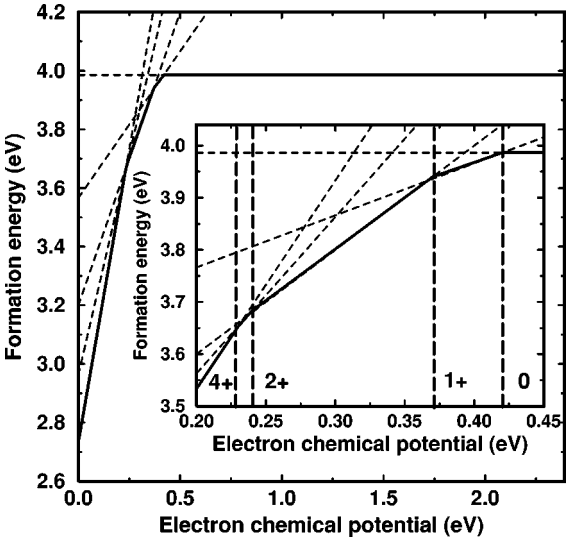

FIG. 1. Formation energy of the fully relaxed silicon antisite in Si-rich 3C SiC. In the inset, two crossing points near the valence band are shown in the range of 0.20–0.45 eV of the electron chemical potential.

defects, which become mobile around ~200 °C. According to Nagesh *et al.*, the experiment clearly indicates that the $E2$ center is not a primary defect, but is formed by the migration of H centers. Up to now, the conclusive interpretation to the microscopic origin of the H or $E2$ centers has not been given.

Itoh *et al.*[6] contemplated that the $H3$ center might be one of the levels of the *silicon vacancy* (V_{Si}). Their argument was based on the tight-binding calculations of Talwar *et al.*,[13] where it was estimated that the silicon vacancy has an ionization level located at 0.54 eV above the valence band maximum. The lowest ionization levels of V_{Si} is $(2+/1+)$, which we could also find after performing a calculation with full ionic relaxations employing a 128 atom-site supercell. We find that the lowest ionization level $(2+/1+)$ of V_{Si} is located at 0.53 eV and the other level $(1+/0)$ at 0.95 eV; both numbers are given with respect to the valence band maximum.[29] Our results for the ideal vacancy give similar results with the linear muffin-tin orbital (LMTO) calculations,[15] but the ionic relaxations pull the ionization levels higher to the band gap. The formation energy of V_{Si} is relatively high: ~8 eV for neutral vacancy. It is experimentally known that V_{Si} is a thermally extremely stable defect in 3C SiC, having a high annealing temperature ~900 °C (Refs. 4,6–8), whereas the H centers are annealed completely at 350 °C. The possibility that the $H3$ center could be due to the silicon vacancy is firmly excluded. Since the ionization levels of the *carbon vacancy*[13,14,22] are situated in the upper half of the band gap, there is no way that the H centers could be due to them either.

According to our calculations neutral *interstitials* in the tetrahedral sites $Si_i(T_C)$, $C_i(T_{Si})$, and $Si_i(T_{Si})$ cannot occur, because they would lead to the occupancy of conduction band states. For the most relevant interstitial $C_i(T_C)$ the calculated formation energy is ~7 eV. For $C_i(T_C)$ we also studied other charge states. The ionization level $(2+/0)$ is ~0.65 eV above the valence band maximum. Since this does

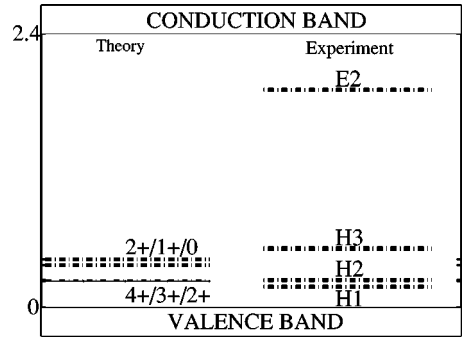

FIG. 2. Calculated ionization levels of Si_C in 3C SiC and the experimental DLTS data from Ref. 28.

not correspond to the measured values of the H centers[28] and because the formation energies for interstitials are very high, the H centers cannot be explained by the interstitials.

It turns out that the *carbon antisite* (C_{Si}) has the lowest formation energy of all studied native defects in C-rich SiC, but in agreement with other published theoretical studies,[12–14] we ascertain that C_{Si} does not introduce any states to the band gap. Thus, C_{Si} is probably the most common native defect in as-grown SiC, but the detected signal from the H centers does not originate from it. The formation energy for C_{Si} reaches its minimum value (3.1 eV) in C-rich material, and maximum (4.3 eV) in Si-rich material. The results for 2H SiC are qualitatively similar. The formation energy of neutral C_{Si} in hexagonal sites is somewhat higher than in cubic sites, 3.4 eV in a material grown under a C-rich atmosphere.

In Si-rich material, among all point defects the *silicon antisite* has the second lowest formation energy of 4.0 eV in 3C SiC and 4.5 eV in 2H SiC. For the Si antisite, in contrast to earlier studies,[12–14] we find that the charge states from 4+ to 0 are possible to occur both in 3C and 2H SiC. The formation energy as a function of the electron chemical potential for Si_C is shown for 3C SiC in Fig 1. Every crossing of the formation energy lines stands for an ionization level, which can be observed experimentally. As can be seen from the figure, Si_C has ionization levels in the band gap in the vicinity of the valence band. For 3C SiC, we determined two principal crossover points: the first is located at 0.2 eV above the valence band maximum and the second 0.2 eV higher. In the first point, the formation energy lines of states Si_C^{4+}, Si_C^{3+}, and Si_C^{2+} cross each other almost in the same point. In the second crossing-point area, Si_C^{2+}, Si_C^{1+}, and Si_C^{0} cross each other in a similar manner.

TABLE I. Calculated nearest-neighbor distances for the antisites C_{Si} and Si_C. The numbers indicate the changes in percent of the ideal bond length (1.865 Å) in 3C SiC. The symmetries of the defects are also given.

C_{Si}^{0}	-11%	-11%	-11%	-11%	T_d
Si_C^{0}	+14%	+14%	+14%	+14%	T_d
Si_C^{1+}	+14%	+14%	+14%	+17%	$\sim C_{3v}$
Si_C^{2+}	+14%	+15%	+14%	+22%	C_{3v}
Si_C^{3+}	+15%	+15%	+17%	+21%	C_{3v}
Si_C^{4+}	+15%	+17%	+20%	+20%	$\sim D_{2v}$

TABLE II. The distances of neighboring atoms from the antisites C_{Si} and Si_C in 2H SiC. The numbers indicate the changes in percent of the corresponding ideal distance (see Fig 3 for the bond numeration). There are three nearest neighbors at 1.865 Å in the plane above (in Fig 3. only two of them are drawn) and one neighbor at 1.88 Å in the plane below. In addition, we examine the distance of a more distant neighbor (3).

Ideal distance	(1) 1.863 Å	(1) 1.863 Å	(2) 1.88 Å	(3) 3.57 Å
C_{Si}^{0}	-9%	-9%	-12%	+0.1%
Si_C^{0}	+11%	+11%	+13%	+0.3%
Si_C^{1+}	+14%	+14%	+13%	+0.8%
Si_C^{2+}	+17%	+21%	+13%	+0.1%
Si_C^{3+}	+19%	+22%	+17%	+1.3%
Si_C^{4+}	+27%	+28%	+20%	+5.1%

Even though in both crossing areas negative-U behavior might take place, it seems that the charge states 3+ and 1+ become occupied for a very limited range of the electron chemical potential. Due to the restricted accuracy of the DFT-LDA method, we cannot rule out either the possibility that these charge states are the most stable for a wider range of the electron chemical potential. A spin-polarized calculation is likely to change the position of spin-unpaired charge states (Si_C^{1+} and Si_C^{3+}) by some tens of meV. Hence, spin polarization is not believed to alter our result in a significant way, but it can make the splitting of Si_C levels (in Fig 2) more pronounced. For 3C SiC the values for the ionization levels are 0.23, 0.24, 0.37, and 0.42 eV above the valence band maximum. For 2H SiC, the ionization levels are calculated to be higher in the band gap. The charge state 3+ is not the stablest for any electron chemical potential value in the band gap. The calculated three ionization levels in 2H SiC are 0.68, 0.81, and 1.0 eV above the valence band maximum.

In 3C SiC, the calculated ionization levels of Si_C correspond well to the experimental levels of H centers (see Fig. 2). They reproduce the two main lines around 0.2 ($H1$ and $H2$) and 0.4 ($H3$) above the valence band maximum. The predicted energy difference between the crossing point areas is around 0.2 eV as the measured energy difference between $H3$ and $H2$ centers is 0.27 eV. Our calculations predict a small splitting for both principal lines; 0.05 eV for the higher one and 0.01 eV for the lower. Experimentally no splitting of the higher level ($H3$) has been observed, whereas in the lower case two lines ($H1$ and $H2$) are separated by 0.06 eV.[28] Even so, the similarity between the calculated ionization levels and experimentally detected levels is striking enough to indicate that H centers in neutron irradiated 3C SiC apparently arise from the presence of silicon antisites. However, it is still possible that the H centers arise from more complex defects, which have not been studied here. Therefore further experimental work is needed to confirm our prediction.

The distances between the antisite atoms and their neighboring atoms are listed for the 3C and 2H structures in Tables I and II, respectively. We give a relative number, measuring the difference between the ideal length and the length in the relaxed structure. For C_{Si} ~11% inwards relaxation takes place, whereas atoms surrounding Si_C move away from it by ~14% of the bond length. For Si_C, the relaxation varies in the range (14–22)% depending on the charge state (see Table I). The relaxations in 2H SiC have common characteristics with 3C SiC (see Table II, Fig. 3). Exceptionally, the relaxations around the hexagonal-site Si_C^{4+} are distinctly larger. The outward relaxation in the nearest-neighbor shell of the antisite atom is ~27% and ~5% for more distant neighbors at 3.57 Å. In 3C SiC, the relaxation reduces the formation energy of C_{Si} by ~1.4 eV. In the case of Si_C, the energy gain in relaxation is ~5–6 eV, depending on the charge state so that the value increases as the electrons are transferred from the antisite. The corresponding values for 2H SiC are slightly larger.

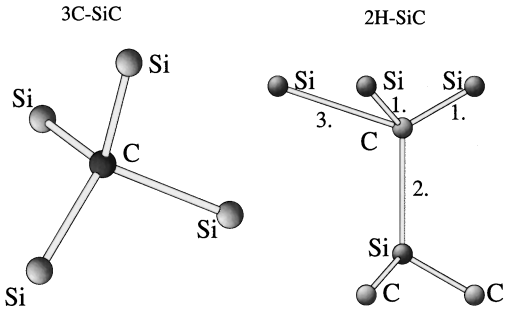

FIG. 3. The local atomic structures for 3C and 2H polytypes of SiC. The bond numeration in 2H SiC is used in Table II.

In summary, our results provide strong evidence that the defect behind the H centers is the silicon antisite, formed in neutron irradiation. Our prediction is based on accurate plane-wave pseudopotential calculations for formation energies and ionization levels of various point defects in 2H and 3C SiC. We find several ionization levels for Si_C in the lowest third of the band gap. Moreover, we obtain a low formation energy for both antisites. Our results give a simple model for H centers, detected in neutron irradiated 3C SiC by Nagesh *et al.*[27] These results support earlier statements that antisites are produced by neutron irradiation and that the signals of H centers are due to point defects. It is also found that carbon antisite has an even lower formation energy than Si_C both in 3C and 2H SiC. This indicates that the electrically and optically inactive C_{Si} is a common defect in silicon carbide.

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[29] The ionization level is defined as a position of the electron chemical potential at which the most stable charge state of the defect changes. The levels arising from the *H* centers are located in the lowest third of the band gap. Thus the ionization levels calculated using the DFT-LDA method do not suffer significantly from the well known underestimation of the band gap in DFT-LDA calculations.